

Structural and ^{57}Fe Mössbauer study of $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$

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Abstract: The synthesis of poly crystalline $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ alloys for $0 \leq x \leq 0.5$ have been investigated. XRD patterns of all specimens reveal the formation of single phase orthorhombic crystal structure recorded using Fe K_α radiation at 300K. The unit cell volume increases with the increase in Ruthenium concentration. ^{57}Fe Mössbauer spectra at 300K and 4.2K for all compositions analysed as a single quadrupole doublet reveal the paramagnetic character. Isomer shift is nearly constant at 300K and 4.2K but there is a increase in quadrupole splitting with increasing ruthenium concentration x for all specimens..

Keywords: ^{57}Fe Mössbauer spectra, Alloys, Magnetism.

1. Introduction

Narrow band gap semiconductor FeSb_2 crystallizes into C18 marcasite type orthorhombic crystal structure where AsRuSb_2 also exist^{1,2}. Magnetic susceptibility of FeSb_2 exhibits diamagnetic to paramagnetic crossover around 100K and it displays large magneto-resistance $[\rho(70\text{kOe}) - \rho(0)]/\rho(0) \approx 2200\%$ in the temperature range $40\text{K} < T_{\text{cr}} < 80\text{K}$. The large magneto-resistance observed in FeSb_2 is of comparable magnitude of the magneto-resistance found in GMR materials^{3,4}. Although Good enough's energy band scheme⁵ for FeSb_2 had been successful in qualitative explanation of electrical

and magnetic properties, it does not account quantitatively for large magneto-resistance and a temperature-induced spin state transition observed by Petrovic *et.al.*^{3,6}. Neutron diffraction studies of FeSb₂ showed no evidence of magnetic ordering down to 4.2K⁷. The electrical measurements on FeSb₂ also hold up the smaller band gap as compared to FeAs₂. There is high conductivity found in FeSb₂ due to promotion of large number of charge carriers across the extremely narrow band gap. Gongalves da silva predicted that FeSb₂ is although non magnetic semiconductor, it may be pushed into a stable magnetic state by the addition of acceptor impurities due to its high magnetic susceptibility⁸. Thus it will be worth testing his hypothesis by substituting the Ruthenium into FeSb₂.

Magnetic susceptibility, Electrical resistivity and magneto-resistance were studied for Cr_{1-x}Ru_xSb₂ ($x = 0$ and 0.1). The electrical measurements show that Cr_{1-x}Ru_xSb₂ ($x = 0$ and 0.1) are semi conductive in the temperature range from 4.2 to 300K⁹. Neutron diffraction measurements were carried out for pseudo binary compounds Cr_{1-x}Ru_xSb₂ ($x = 0.05$ and 0.2) with a Marcasite-type structure at temperatures from 15 to 260K. The results show that their magnetic structures are antiferromagnetic ones in which the magnetic unit cell requires a doubling of the b- and c-axes of the orthorhombic chemical cell and both magnetic moment and the Néel temperature decreases with x and appear to be zero around $x = 0.4$. The results are discussed comparing with those for the compounds Cr_{1-x}Ru_xSb₂. Fe_{1-x}Mn_xSb₂ system for $0 \leq x \leq 0.2$ and Fe_{1-y}Cr_ySb₂ system for $0 \leq y \leq 0.97$ Mössbauer studies have been performed at 300K and found single quadrupole doublet¹⁰⁻¹². The FeSb₂ is a mysterious material with peculiar colossal thermopower of about 45mV/K at 10K¹³, and has large Seebeck coefficient at cryogenic temperatures¹⁴, thermoelectric transport coefficient¹⁵ and unusual temperature dependence of thermoelectricity¹⁶.

We have therefore attempted to synthesize Fe_{1-x}Ru_xSb₂ for $0 \leq x \leq 0.5$ to check the solid solubility of Ru for Fe into marcasite type structure of FeSb₂ and also to explore in detail the anisotropic electronic, electrical and magnetic properties of Fe_{1-x}Ru_xSb₂. In this present paper, We report here for the first time the details of the synthesis and investigations of these compounds using X-ray powder diffraction and ⁵⁷Fe Mössbauer spectroscopic techniques at 300K and 4.2K.

2. Experimental Details

2.1 Synthesis

High purity ($\approx 99.999\%$) elements (Fe, Sb and Ru) were weighed in stoichiometric proportion corresponding to Fe_{1-x}Ru_xSb₂ for system $x = 0.0$,

0.1, 0.3 and 0.5 and were sealed under vacuum ($\approx 10^{-2}$ Torr) in quartz ampoule. The ampoules were kept in Kanthal wire wound resistive furnace. Initially the temperature was slowly raised from 300K to 1273K in the time interval of about 30 hours to ensure solid state diffusion of Ru, Fe and Sb. The temperature was fixed at 1273K for 30 hours which ensured the complete melting and then the ampoules were quenched into ice water. The furnace temperature was controlled by a temperature controller (within ± 10 K). The black ingot, thus, obtained was crushed into fine powder and put again into an evacuated quartz ampoule and was annealed at 873K for 15 days and then quenched into water. The annealed samples were crushed into fine powder using agate mortar and pestal in methanol and dried at 350K. We have synthesized four compositions corresponding to $x = 0.0, 0.1, 0.3$ and 0.5 of the $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$.

2.2 X-ray Diffraction

X-ray powder diffraction patterns were recorded at 300K for these specimens using a Phillips 1840 model diffractometer (operated at 30 kV and 30 mA) by varying the 2θ angle in the step of 0.02° from 10° to 90° . XRD data were analyzed using a standard program¹⁷ called powder X.

2.3 Mössbauer Experiments

^{57}Fe Mössbauer experiments at 300K were performed in the transmission geometry and in the constant acceleration mode. The data were collected on to the multi channel analyser controlled by a computer software (MCD/PC) using 512 channels. The Mossbauer spectra corresponding to the all specimens were calibrated using natural iron foil. Each Mössbauer absorber was prepared by using 40 mg/cm^2 of the synthesized specimen. The observed Mössbauer spectra were fitted using a standard data analysis program using lorentzian mathematical function. ^{57}Fe Mössbauer experiments at 4.2K were carried out using liquid Helium cryostat. The temperature was controlled to an accuracy of ± 1 K with the help of temperature controller. The absorber was filled in an annular copper ring of ~ 16 mm diameter and 1 mm in depth this ring was kept at the centre of cryostat.

3. Result and Discussion

3.1 X-ray diffraction analysis

Fig. 1 shows the XRD powder patterns for $x = 0.1, 0.3$ and 0.5 for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ alloys. The experimental peaks were indexed using Dong's indexing program¹⁷. For all the specimens, the large intensity peaks observed corresponding to reflections (011), (111), (211), (221) and (002). We present

here the details of the observed and analyzed X- ray powder diffraction data using Dong’s programme for $\text{Fe}_{0.9}\text{Ru}_{0.1}\text{Sb}_2$, $\text{Fe}_{0.7}\text{Ru}_{0.3}\text{Sb}_2$, and $\text{Fe}_{0.5}\text{Ru}_{0.5}\text{Sb}_2$. No peak corresponding to either Fe or Ru or Sb or their binary phase was observed confirming that there does not exist any elemental or binary phase impurities.

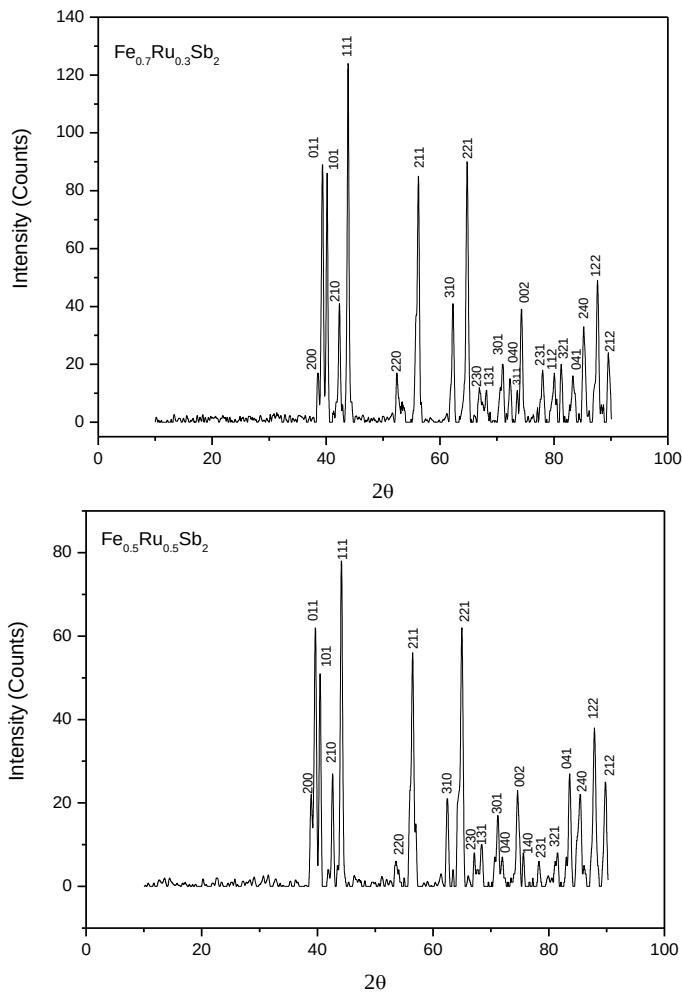


Figure 1. XRD Powder patterns (300K) for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ system.

Table 1. Lattice parameters and unit cell volume (300K) for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ System for $0.0 \leq x \leq 0.5$.

$\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$	a (Å)	b (Å)	c (Å)	v (Å) ³
0.0 ¹⁸	5.840	6.540	3.203	122.334
0.1 ¹⁸	5.857	6.537	3.233	123.782
0.3	5.873	6.549	3.219	123.810
0.5	5.875	6.556	3.218	123.946

Fig. 2 displays the lattice parameters (a , b , c) and the unit cell volume (V) plotted against Ru atomic percentage. It reveals increase in cell volume of lattice with ruthenium concentration x . the lattice parameters for FeSb_2 obtained from analysis match well with those reported earlier. Table 1 shows the lattice parameters and cell volume for the specimens of the series. It reveals an increase in lattice parameters and also in unit cell volume with increasing Ru concentration.

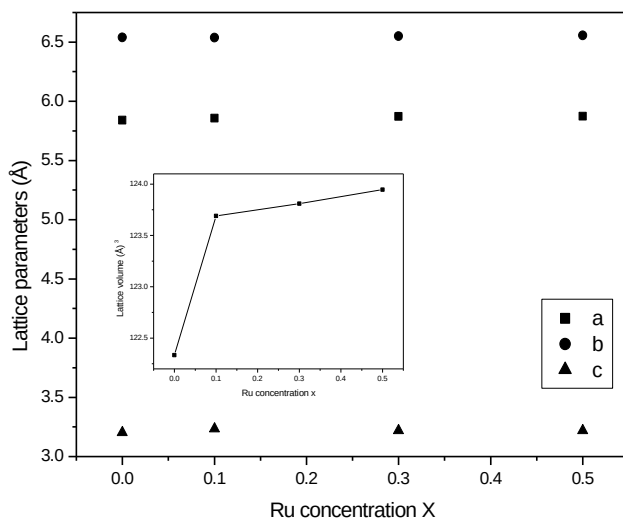


Figure 2. Plot of Lattice parameters with Ru concentration (inset shows the unit cell volume) for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$

3.2 ^{57}Fe Mossbauer spectroscopy

Fig. 3 exhibits the ^{57}Fe Mössbauer spectra observed at 300K for the specimens with $x = 0.0, 0.1, 0.3$ and 0.5 for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ alloys and Fig. 4 shows ^{57}Fe Mössbauer spectra observed at 4.2K for the $\text{Fe}_{0.9}\text{Ru}_{0.1}\text{Sb}_2$. The experimental data points have been shown by dots whereas the solid line is the computed envelope of the single quadrupole split doublet.

The percentage absorption ranges between 5% and 12%, the largest being for FeSb_2 . Table 2 gives the values of Mössbauer parameters viz., isomer shift (IS), quadrupole splitting (QS), line width (full width at half maximum, LW) and χ^2 , the goodness-of-fit-parameter respectively at temperature 300K and 4.2K. The line width of the specimens ranges between 0.380 mm/s – 0.420 mm/s at 300K and 0.234 mm/s - 0.247 mm/s at 4.2K. This width compared with the width for natural iron absorber at 300K and 4.2K (≈ 0.28 mm/s) justifies the fitting of single quadrupole doublet with acceptable χ^2 values corresponding to one crystallographic iron site, namely $2a$ site, in the orthorhombic FeSb_2 structure.

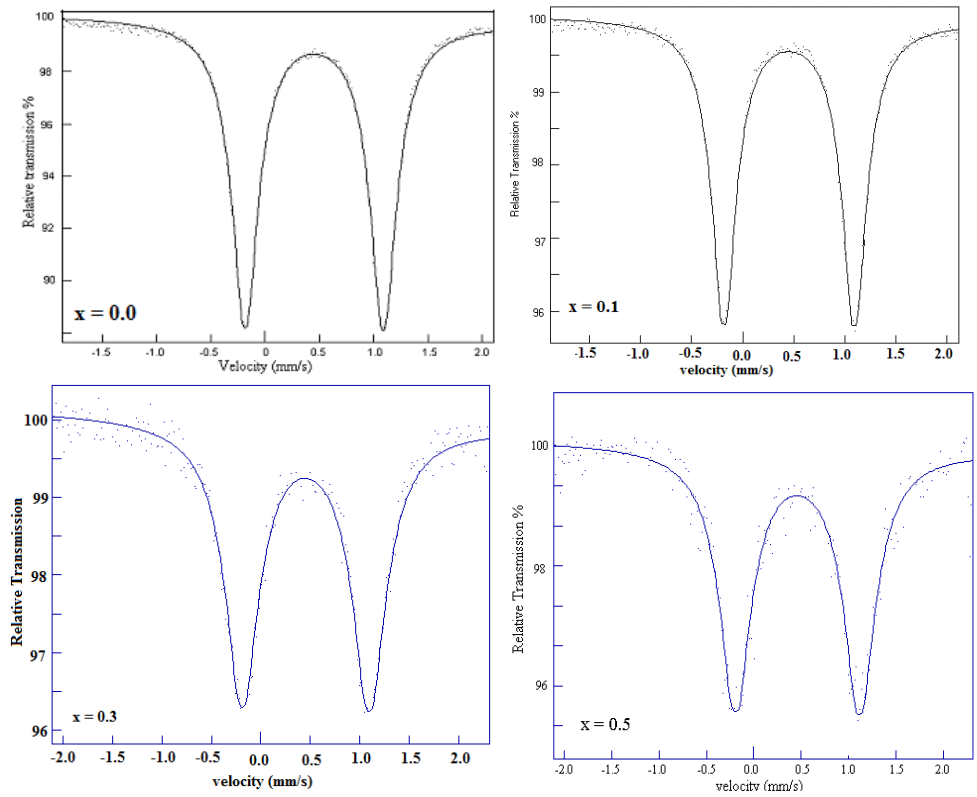


Figure 3. ^{57}Fe Mössbauer spectra observed at 300K for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ system.

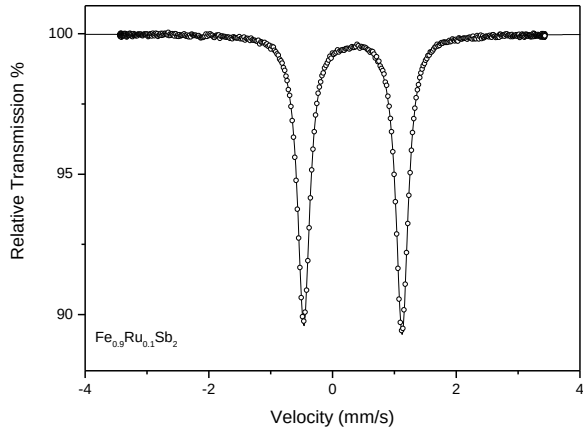


Figure 4. ^{57}Fe Mössbauer spectra observed at 4.2K for $\text{Fe}_{0.9}\text{Ru}_{0.1}\text{Sb}_2$

The Mössbauer spectra for these specimens indicate paramagnetic character at 300K and 4.2K as neither hyperfine structure nor any sizable line broadening is observed. The Mössbauer parameters, IS and QS for FeSb_2 match well with our earlier reported work^{18,19}. Table 2 reveal that isomer shift

does not change much upon Ru substitution. Assuming that for every Fe ($3d^6$) atom replacement by a Ru ($4d^6$) atom, the 3d shielding effect due to the 4d electronic population should get equal. This should then lead to no change in s-electron density at iron nucleus resulting in same isomer shift. However, it is to be noted that Ru affects only the second nearest neighbour site of iron. This fact together with the covalent nature of Fe-Sb-Fe(Ru) bonds should be responsible for the observed constancy of isomer shift values with respect to increase in Ru concentration. This observation is similar to the reported constancy of the isomer shift in $\text{Fe}_{1-x}\text{T}_x\text{Sb}_2$ systems (for $\text{T} = \text{Cr}, \text{Ni}$, for $0 \leq x \leq 0.2$) with respect to increase in transition metal atom (T) concentration²⁰. The isomer shift values further suggest the low spin state of iron in these specimens.

Table 2. ^{57}Fe Mössbauer parameters at 300K and 4.2K for $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ system, Isomer shift δ is given with respect to $\alpha - \text{Fe}$.

x	IS (mm/s) (± 0.000)		QS (mm/s)(± 0.000)		LW (mm/s) (± 0.001)	
	300K	4.2K	300K	4.2K	300K	4.2K
0.0 ¹⁸	0.452	0.320	1.250	1.570	0.380	0.247
0.1 ¹⁸	0.452	0.329	1.262	1.589	0.381	0.237
0.3	0.450	0.328	1.283	1.591	0.420	0.239
0.5	0.458	0.331	1.308	1.598	0.413	0.234

Coming to the value of quadrupole splitting, it increases upon increasing Ru concentration; for $x = 0.5$ specimen the change in QS is more than 4.64 % and 1.78% respectively at 300K and 4.2K as compared to pure FeSb_2 . The Ru substitution for Fe leads to increase in the lattice parameters and the unit cell volume may indicate that the larger distortion of the iron octahedral site. This should increase the lattice contribution to quadrupole splitting which in turn should increase the quadrupole splitting with increasing the Ru concentration. Thus in this system $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ Fe replaced by Ru, one can expect the valence electron contribution in $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$ to the quadrupole splitting to increase as 4d electronic population increases by replacing one Fe atom by either Ru. The quantitative determination of either lattice or electronic contribution to quadrupole splitting require detailed studies of these alloy systems by single crystal X-ray diffraction and other spectroscopic techniques yielding details of Fe-Sb-Ru bond lengths and bond angles.

4. Conclusion

XRD analysis indicates that Ru can be substituted for Fe upto 50% atomic percentage system remaining orthorhombic crystal structure. The unit cell

volume increases with the increase in Ru concentration x . The ^{57}Fe Mossbauer spectra for all compositions reveals low spin state of Fe and the existence of the paramagnetic character at 300K and 4.2K. The IS values do not change and QS values increase with Ru concentration for the $\text{Fe}_{1-x}\text{Ru}_x\text{Sb}_2$.

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